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SELECTIVITY OF HERBICIDES

A. S. CRAFTS

With the introduction of new organic chemicals, the use of selective herbicides is finding broader application. Stimulated by war conditions, their use offers a promising method for increasing efficiency and reducing drudgery of agricultural production.

Early work on selective herbicides is reviewed by ÅSLANDER (1), and by ROBBINS, CRAFTS, and RAYNOR (17). This paper considers selectivity from a broader viewpoint, discussing the selective killing of annual weeds in crops of the family Umbelliferae by oils, the control of annuals and shallow-rooted perennials among deep-rooted perennial crops, and the selective use of growth regulators as sprays and soil amendments.

Plants differ in many ways; their surfaces vary in form and chemical composition; some are easily wet by aqueous sprays; others are difficult to wet. Surface coatings vary in permeability, and protoplasm responds specifically to different chemicals. The gross structure of plants varies in such a way that the meristematic tissues of some are exposed and vulnerable to sprays, others have their growing points protected. Because of these differences certain weeds may be destroyed in growing crops with little or no injury to the latter.

The nature of selectivity

The surface of cereal leaves is usually minutely ridged, that of broad-leaved weeds such as Brassica, Raphanus, and Amsinckia species is smooth. The cuticle of cereal leaves is silicious, waxy, or coated with minute particles of waxy bloom; that of the above weeds is more susceptible to wetting with aqueous sprays. The leaves of cereal crops tend to be upright; those of broad-leaved weeds are flat and horizontal. The growing points of cereals are located at the base of the plant and are protected by older leaves; the same applies to onion. Growing points of broad-leaved weeds are terminal and exposed.

Roots of many annual and shallow-rooted perennial weeds are located in the top soil layer; those of deep-rooted plants may extend many feet into the subsoil. Examples are foxtail (*Hordeum* spp.), shepherd's purse (*Capsella bursa-pastoris*), plantains (*Plantago* spp.), and chicory (*Cichorium intybus*) as weeds in alfalfa. Finally, differences in the susceptibility of weeds and crops depending upon the reactivity of the protoplasm may be illustrated by annual blue grass (*Poa annua*), mustards, and shepherd's purse; such weeds are commonly killed by stove oil,¹ whereas carrots and celery are unharmed.

¹ Stove oil is a light fuel oil used for domestic heating in the Western United States. It is an unrefined fraction of western crudes conforming to the following specifications:

Gravity, API (Amer. Petrol. Inst.) 37.6° to 38.7°.

Viscosity (Saybolt Universal) at 100° F., 31 to 33 secs.

Flash point (Pensky-Martens closed cup) 134°-140° F.

All these plants are thoroughly wet by the spray, which penetrates the carrot and celery plants, as evidenced by their oily flavor. Evidently the selectivity shown between grasses and broad-leaved plants by the growth-regulating chemicals is of the same nature; it is displayed both by the salts of dichlorophenoxyacetic acid in aqueous solution and by the esters in nontoxic oil. Selectivity is shown by plants both after treatment of the roots through the soil (18) and after spraying of the tops (9, 14).

The action of selective herbicides is relative, depending on the concentration or dosage applied. No case of absolute selectivity is known; the toxicant will always kill both weed and crop species if brought into intimate contact with the plants in sufficient concentration. Herbicides known for their general contact toxicity (ability to kill all plant species) are selective if applied to weeds and crop plants in a series of concentrations.

Experimental work

Data presented are samples from much experimentation over several years. They have been selected to illustrate the general principles just presented. Thus the problem of relative toxicity as compared with absolute or universal toxicity was investigated. Early work (4) proved the efficacy of sodium chloride, iron sulfate, copper sulfate, and even sodium arsenite as selective herbicides. On the other hand, sodium arsenite was used as a general contact "weed killer" (21) and soil sterilant (12, 19). Evidently arsenic could serve as either a selective or a general contact herbicide. Studies on selective herbicides in cereal-crop experiments at Davis, California, in the spring of 1932 included plots sprayed with sodium arsenite solutions (table I). The plants averaged about 6 inches in height at the time of spraying.

The 4 per cent. solution killed all the barley and weeds. The 2 per cent. solution killed all the weeds and injured the barley, but the latter recovered rather quickly. The 1 per cent. solution injured the barley slightly and failed to eliminate fiddleneck completely. The lower concentrations injured the weeds but did not control them sufficiently to prevent reseeding. Plots 2 and 3 had materially increased yields; plot 4 was somewhat better than the checks.

Evidently sodium arsenite, ordinarily regarded as a general contact weed killer, will act selectively if applied at the proper concentration.

Practically all inorganic salts are somewhat toxic to plants if sufficiently concentrated solutions are applied to the foliage. Many are low in toxicity and will not kill all species, even if applied in saturated solution; most of

Distillation temperatures:

Initial boiling point	335° to 380° F.
10 per cent. point	380° to 390° F.
90 per cent. point	480° to 515° F.
End point	535° to 570° F.
Water and sediment	0.0 to trace
Sulfur content	0.13% to 0.68%

these would be of no practical value as herbicides. The following list enumerates salts that have been tried and found useful: iron sulfate, copper sulfate, copper chloride, copper nitrate, sodium chloride, sodium chlorate, sodium arsenite, barium chlorate, sodium chromate, sodium dichromate, sodium nitrate, sodium bisulfate, nickel sulfate, ammonium sulfate, zinc sulfate, potassium chloride, magnesium chloride.

Besides these, many other salts have been tested (5). Arsenic acid and sulfuric acid have also given practical results; in fact, for several years before the dinitro compounds were introduced, sulfuric acid led as a selective herbicide, particularly in cereal crops.

TABLE I

TOXICITY OF SODIUM ARSENITE SPRAYS TO MUSTARD, FIDDLENECK,* AND BARLEY.
INJURY IS EXPRESSED AS PERCENTAGE OF DAMAGE TO FOLIAGE COMPARED
WITH UNTREATED CHECKS. ALL PLOTS 1 SQUARE ROD IN AREA.
TREATMENT FEBRUARY 19, 1932

PLOT NO.	ARSENIC CONCENTRATION†	INJURY BY MARCH 1, 1932			INJURY BY APRIL 1, 1932		
		BARLEY	MUSTARD	FIDDLE-NECK	BARLEY	MUSTARD	FIDDLE-NECK
	%	%	%	%	%	%	%
1	4.00	100	100	100	100	100	100
2	2.00	10	100	100	0	100	100
3	1.00	5	100	90	0	100	90
4	0.50	0	95	85	0	95	75
5	0.25	0	90	75	0	90	50
6	0.125	0	75	10	0	50	0

* The common name fiddleneck is used here to designate *Amsinckia douglasiana*, a common grainfield weed of central California.

† Percentage of As_2O_3 by weight.

Selectivity of these salts and acids in aqueous solution is largely a result of differential wetting; differences in the surface coating of the plants and in the form and orientation of leaves, rather than chemical tolerances, account for the differences in injury. If wetting agents are added to such solutions, selectivity is reduced; the crop plants may be severely injured.

In addition to the protection afforded plants because of their ability to resist wetting, other mechanisms may be involved. For instance, if wetting agents are added to sulfuric acid sprays, grass leaves will be severely damaged; stems, on the other hand, may show little injury; and new leaves, developing from growing points buried deeply in the centers of the stems near the crown, may be unharmed. This type of selectivity, dependent upon structure, became evident when wetting agents were added to sulfuric acid in an effort to develop a general contact herbicide. Besides grasses, *Erodium* species in the rosette showed resistance; and in this case, again, selectivity was based upon structure, not upon wettability or any other chemical characteristic. As with sodium arsenite, sulfuric acid will kill all plants if applied in sufficient concentration; at intermediate concentrations (about 10 per

cent. by weight) it readily kills broad-leaved plants but not grasses; and at low concentrations (about 3 per cent.) it will kill dodder, small seedlings of mustards, chickweed, and the like. Toxicity again ranges from total to zero, depending upon concentration, plant species, and environmental factors that determine the susceptibility of plants to acid injury.

THE DINITRO COMPOUNDS

The introduction of Sinox (the sodium salt of dinitro ortho cresol) in 1938 started a new phase in the use of selective herbicides. Experiments in California (20) proved this material to be highly selective, noncorrosive, and far less toxic to animals than sodium arsenite (16). Soon after its commercial introduction, Sinox was used extensively on the Pacific Coast. In Oregon (10) it was tried in combination with other chemicals, notably ammonium sulfate, calcium cyanamid, sodium bisulfate, sulfuric acid, sulphamic acid, and ammonium sulfamate. These supplementary chemicals were first added to test the possibility of applying a fertilizer along with the herbicide. All those listed above increased the effectiveness of Sinox, ammonium sulfate producing the most outstanding results. It soon became evident that an amount of this chemical insufficient to give a fertilizing effect greatly increased the activity of the Sinox, and that crop increases were incommensurate with the total nitrogen applied. Furthermore, comparable results were obtained by the use of sodium bisulfate. Since toxicity of sodium dinitro ortho cresylate was increased when these acid salts were added, such addition soon became known as "activation."

TABLE II

CROPS IN WHICH SELECTIVE WEED CONTROL MAY BE PRACTICED, AND WEEDS THAT MAY BE KILLED BY SELECTIVE HERBICIDES IN AQUEOUS SOLUTION

CROPS	
Wheat	Corn
Barley	Onions
Oats	Garlic
Rye	Ryegrass
Flax	Fescue
Peas	
WEEDS	
Mustards, <i>Brassica nigra</i> and <i>B. arvensis</i>	
Wild turnip, <i>Brassica campestris</i>	
Hedge mustard, <i>Sisymbrium</i> spp.	
Fiddleneck, <i>Amsinckia</i> spp.	
Fan weed, <i>Thlaspi arvense</i>	
Pennycress, <i>Thlaspi perfoliatum</i>	
Russian thistle, <i>Salsola kali</i>	
Prickly lettuce, <i>Lactuca scariola</i>	
Cornecockle, <i>Agrostemma githago</i>	
Shepherd's purse, <i>Capsella bursa pastoris</i>	
Small nettle, <i>Urtica urens</i>	
Nightshade, <i>Solanum nigrum</i>	
Wild buckwheat, <i>Polygonum convolvulus</i>	
Lamb's-quarter, <i>Chenopodium album</i>	
Hungerweed, <i>Ranunculus arvensis</i>	

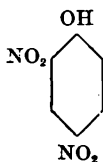
In California, work on the activation of Sinox (7) has indicated the nature of the chemical reaction involved. Besides demonstrating that Sinox could be activated, HARRIS and HYSLOP (10) showed conclusively that ammonium sulfate or calcium cyanamid could be applied simultaneously with the selective herbicide and that the enhanced toxicity resulted in excellent control of weeds, including some species which Sinox would ordinarily not affect. They also showed that sulfamic acid and ammonium sulfamate would activate Sinox. More recently aluminum sulfate has been added to the list of activators.

Not only have the field trials demonstrated the efficiency of Sinox as a selective herbicide; they have increased the number of crops in which this kind of control may be practiced. Table II lists the known crops in which weeds may be treated selectively and the principal weeds that may be killed by selective herbicides. As this list shows, many new crops have been added since Bolley's early experiments with selective herbicides. The question naturally arises: how far can this list be extended? There are two chief ways of improving selective herbicides: (1) by increasing the toxicity so that dosage can be reduced, and (2) by widening the selectivity or extending it to entirely new groups of plants. Both these improvements have been accomplished in recent years.

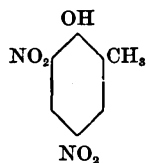
INCREASED TOXICITY

The first step in increasing the toxicity of the dinitro compounds was the use of acid salts as activators in the way mentioned above. The next step was to test the ammonium salt of dinitro ortho cresol. It proved as toxic as the activated sodium salt. Since the ammonium salt is not as highly inflammable as the dry sodium salt, it is a water-soluble dry powder that may be used under field conditions. Its use reduces the weight of material required per acre from 10 pounds (the approximate weight of 1 gallon of Sinox) to 3 pounds. This effects a real saving in transportation and provides a more convenient form for handling the chemical.

Dinitro phenol has the formula



The formula of dinitro ortho cresol is



Since the latter is much more toxic than the phenol, it seems reasonable that lengthening the aliphatic chain might further increase toxicity. This has

proved to be true. Testing of the 2,4 dinitro compounds of phenol, o-methyl, o-ethyl, o-isopropyl, o-secondary butyl, and o-secondary amyl phenol, respectively, showed that toxicity increases through the first five and drops slightly in the sixth. Table III from CRAFTS (6) illustrates this relation. The ammonium salts of these compounds are water-soluble, and ammonium dinitro ortho secondary butyl phenylate is three to four times as toxic as the corresponding cresylate. It is less irritating than the cresylate, readily soluble in water, and its density is such that $\frac{3}{4}$ pound finely powdered has a volume of about 1 pint. This, dissolved in 100 gallons of water, will control mustards and similar grain-field weeds in an average acre of grain. Further increases in the toxicity of selective herbicides will be of little benefit unless accompanied by a decrease in cost because the volume of material mentioned above is about as low as is convenient to handle.

TABLE III
SOLUBILITY IN OIL AND RELATIVE TOXICITY* OF DINITRO COMPOUNDS†

CHEMICAL	SOLUBILITY‡ IN KEROSENE AT 20° C.	TOXICITY*	$\frac{\text{CHAIN WEIGHT}}{\text{TOTAL MW}} \times 100$
	% (approx.)		
Dinitro phenol	0.14	38	0.0
Dinitro-o-cresol	0.58	64	7.5
Dinitro-o-ethyl phenol	2.39	75	13.6
Dinitro-o-isopropyl phenol	3.43	90	18.9
Dinitro-o-secondary butyl phenol	Miscible	100	23.6
Dinitro-o-secondary amyl phenol	Miscible	90	27.8

* Toxicity in arbitrary units has been calculated to a basis of 100 per cent. for dinitro-o-secondary butyl phenol, the most toxic of the six compounds. This toxicity would require concentrations of approximately 0.5 per cent. on grasses and 0.125 per cent. on broad-leaved weeds if applied in nontoxic oil or oil emulsion under the conditions of these experiments.

† Table taken from CRAFTS (6).

‡ Solubility is higher in more polar solvents. The aromatic and olefin contents of petroleum fractions largely determine their solvent power for the nitrophenols.

BROADENING SELECTIVITY; THE SELECTIVE OILS²

Discovery of the selective action of certain petroleum fractions has added a whole new group of crops that may be weeded chemically; those belonging to the family Umbelliferae. Principal among these are carrots and celery; others include parsnip, parsley, dill, and caraway. Guayule will tolerate stove oil and low dosages of diesel oil.³

² Work on the herbicidal properties of oil in California has been cooperative between the Botany and Chemistry Divisions of the College of Agriculture. H. G. REIBER and H. W. ALLINGER of the Chemistry Division have aided in the experimental work reported here.

³ Diesel oil is a medium grade fuel oil, used for diesel motors. It is not highly refined and it is toxic to most plants. The following specifications are used in purchasing diesel oil for spraying fire strips along California highways:

Gravity (A.P.I.) at 60° not less than 27° F.

Viscosity (Saybolt Universal) at 100° F. not over 50 secs.

Selectivity of petroleum oils is evident among weeds as well as crop plants. Fennel (*Foeniculum vulgare*), snake root (*Sanicula* spp.) and poison hemlock (*Conium maculatum*) are three Umbelliferae that escape injury from oil. Pineapple weed (*Matricaria suaveolens*), groundsel (*Senecio vulgaris*), purslane (*Portulaca oleracea*), and yellow star thistle (*Centaurea solstitialis*) are somewhat tolerant, especially in the rosette stage. Grasses and many broad-leaved annuals are readily killed by spraying with oils.

According to studies on the toxicity of oils, the aliphatic hydrocarbons are nontoxic; the aromatic hydrocarbons and olefinic compounds are largely responsible for oil injury (8). Of the aromatic and olefinic compounds that occur naturally in petroleum, those boiling below about 200° F. cause a rapid killing of plant tissue, termed acute toxicity; those boiling above 200° F. act more slowly but cause a more profound injury—the so-called chronic toxicity (8). Selective toxicity of the type caused by stove oil is largely acute; and experiments have shown that oil fractions even lighter than stove oil are preferable as carrot sprays because they are more toxic and leave less residual odor and flavor in the vegetable.

There is no sharp point of distinction between compounds causing acute and chronic injury. The temperature of 200° F. represents the low point of a range. Compounds boiling below 200° F. show acute toxicity; those boiling above about 400° F. show chronic toxicity. In the range between 200° and 400° F., compounds will exhibit some of each type provided the dosage is adjusted so that acute toxicity will not kill the plants.

Selectivity and toxicity of oil fractions vary with the boiling range. Carrots tolerate the light oils boiling below 200° F. Under similar growing conditions, flax and onions are injured by such light oils, but the latter crops will tolerate low concentrations of aromatic and olefinic toxicants in the boiling range of kerosene, namely 200° to 400° F. For this reason kerosene will not injure flax and onions; but even its low content of chronic toxicant is sufficient to kill seedling grasses such as wild oats and barley. One can therefore obtain selective killing of these grasses in flax and onions in the greenhouse at will. In some cultures the same grasses were killed without injury to wild mustard. This is the reverse of the selectivity shown by dinitro compounds. In fact, the oils seem to have a specific selectivity against grass species, in contrast to broad-leaved plants.

Certain plants tolerate the chronic toxicants of oils as heavy as diesel oil. Notable among these are guayule and fennel. Light dosages of diesel oil are regularly used for controlling weeds in guayule crops. Where this oil has been used annually to kill weeds on fire strips along highways in California, fennel has been uninjured and has grown, unlimited by competition, occupying many sprayed areas completely.

Selective toxicity of oils differs from that of aqueous solutions because

Flash point (PMCC) not less than 150° F.

Distillation, 90% point not over 680° F.

Water and sediment not over a trace.

wetting is not involved. Since the tops of the plants are thoroughly wet by the oil sprays, the absence of injury to the tolerant crops and weeds must be characteristic of their protoplasm.

Selectivity of oils, again, is relative; if the toxicant is used in high enough concentration, all plants are killed. This point was proved experimentally in two ways.

TABLE IV

TOXICITY OF XYLENE, ISOPARAFFIN, AND THEIR COMBINATIONS TO CARROTS, MUSTARD, AND FOXTAIL (*Hordeum murinum*). DATE OF APPLICATION
MARCH 14, 1945, 9: 00-10: 00 A.M.

OIL MIXTURE		INJURY—PERCENTAGE OF UNTREATED CHECKS					
XYLENE	ISO-PARAFFIN	DATE OF OBSERVATION					
		MARCH 14, 1945			MARCH 15, 1945		
		CARROTS	MUSTARD	FOXTAIL	CARROTS	MUSTARD	FOXTAIL
%	%	%	%	%	%	%	%
100	0	95	100	100	100	100	100
80	20	90	95	100	95	100	100
60	40	80	95	95	85	95	95
50	50	20	95	90	25	95	95
40	60	5	95	75	5	95	80
0	100	0	0	0	0	0	0
		MARCH 16, 1945			MARCH 17, 1945		
100	0	100	100	100	100	100	100
80	20	95	100	100	95	100	100
60	40	85	95	100	85	100	98
50	50	35	95	98	40	95	98
40	60	5	95	90	5	95	95
0	100	0	0	0	0	0	0
		MARCH 19, 1945			MARCH 21, 1945		
100	0	100	100	100	100	100	100
80	20	90	100	100	90	100	100
60	40	75	100	95	75	100	95
50	50	40	95	100	40	100	100
40	60	5	98	95	5	98	98
0	100	0	0	0	0	0	0
		MARCH 26, 1945			MARCH 31, 1945		
100	0	100	100	100	100	100	100
80	20	80	100	99	60	100	99
60	40	70	100	98	50	100	98
50	50	30	98	100	15	98	100
40	60	0	98	98	0	95	99
0	100	0	0	10	0	0	10

First, the aromatic compound, xylene, was used straight, and also in a series of dilutions with a relatively nontoxic aliphatic hydrocarbon. Either pure xylene or xylene in concentrations above 60 per cent. was fatal to all plants. At concentrations between 60 and 40 per cent., it killed weeds without injuring carrots. Table IV presents the results of one such experiment.

Second, aromatic and olefinic compounds extracted from petroleum fractions were used pure and in dilution series. The results were similar to those reported with xylene (tables V and VI). These petroleum extracts, however, are higher in toxicity than xylene. For this reason, straight gasoline containing around 20 per cent. of aromatic and olefinic compounds is highly selective whereas xylene, to produce the same results, must be used at a higher concentration.

TABLE V

TOXICITY OF OLEFINIC FRACTION IN DILUTION WITH NORMAL CETANE TO CARROTS, FLAX, AND FOXTAIL. DATE OF APPLICATION APRIL 25, 1945

OIL MIXTURE		INJURY—PERCENTAGE OF UNTREATED CHECKS					
HEAVY OLEFINIC FRACTION	CETANE	APRIL 26, 1945			APRIL 28, 1945		
		CARROTS	FLAX	FOXTAIL	CARROTS	FLAX	FOXTAIL
%	%	%	%	%	%	%	%
50	50	5	20	50	10	50	85
45	55	5	10	30	20	40	70
40	60	0	5	20	5	20	60
35	65	0	0	10	0	10	30
30	70	0	0	5	0	2	20
25	75	0	0	0	0	1	10
		MAY 1, 1945			MAY 3, 1945		
50	50	20	90	100	10	95	100
45	55	20	75	80	15	90	90
40	60	10	65	75	10	75	80
35	65	0	35	30	0	40	40
30	70	0	10	25	0	10	20
25	75	0	5	15	0	5	10
		MAY 5, 1945			MAY 7, 1945		
50	50	10	95	100	15	95	100
45	55	15	90	95	15	90	95
40	60	10	80	85	15	80	90
35	65	0	50	75	5	60	80
30	70	0	15	20	0	20	20
25	75	0	5	10	0	5	10
		MAY 11, 1945			MAY 14, 1945		
50	50	15	95	100	10	90	100
45	55	10	90	100	5	80	100
40	60	10	80	95	5	70	100
35	65	0	60	90	0	50	100
30	70	0	15	40	0	10	75
25	75	0	0	20	0	0	40

The selective nature of stove oil is purely fortuitous. It depends on the fact that this fraction is within a boiling range which largely excludes compounds toxic to carrots. Stove oil for carrot spraying should have an API gravity rating of $38.0 + ^\circ \text{F}$. A sample of such oil rating 34.7° severely injured carrots in the field. This observation proves that stove oil is just at the limit of gravity for carrot spraying. A lighter oil is superior; not

only does it have higher selectivity, but it is more volatile and hence leaves less objectionable odor and flavor. Experiments with third-structure gasoline as a carrot spray have proved these statements to be correct. Third-structure gasoline is the heaviest and consequently the least expensive grade sold commercially as an automobile fuel.

In the Eastern United States no fraction comparable with stove oil is manufactured. In attempting to duplicate such a fraction, LACHMAN (13)

TABLE VI

TOXICITY OF HEAVY AROMATIC FRACTION IN DILUTION WITH NORMAL CETANE TO CARROTS, FLAX, AND FOXTAIL. DATE OF APPLICATION APRIL 25, 1945

OIL MIXTURE		INJURY—PERCENTAGE OF UNTREATED CHECKS					
HEAVY AROMATIC FRACTION	CETANE	APRIL 26, 1945			APRIL 28, 1945		
		CARROTS	FLAX	FOXTAIL	CARROTS	FLAX	FOXTAIL
%	%	%	%	%	%	%	%
40	60	5	50	50	10	85	90
35	65	0	5	60	5	25	90
30	70	0	0	30	0	10	60
25	75	0	0	15	0	10	40
20	80	0	0	10	0	5	25
0	100	0	0	0	0	0	10
		MAY 1, 1945			MAY 3, 1945		
40	60	15	95	100	15	95	100
35	65	5	80	100	5	80	100
30	70	0	70	90	0	70	95
25	75	0	50	75	0	60	80
20	80	0	20	50	0	20	60
0	100	0	0	0	0	0	0
		MAY 5, 1945			MAY 7, 1945		
40	60	15	95	100	10	95	100
35	65	5	80	100	5	80	100
30	70	0	70	95	5	70	100
25	75	0	60	85	0	60	90
20	80	0	20	75	0	25	80
0	100	0	0	0	0	0	0
		MAY 11, 1945			MAY 14, 1945		
40	60	10	95	100	5	90	100
35	65	5	90	100	0	90	100
30	70	5	75	100	0	75	100
25	75	0	60	90	0	60	75
20	80	0	25	80	0	25	50
0	100	0	0	0	0	0	0

recommends oils of the "straight-run petroleum naphtha type" having "an aromatic content of approximately 15 per cent." Some such oils are "Sovasol No. 5," "Stoddard Solvent," "Mineral spirits," and "Sun Spirits." These are fractions used in industry as paint thinners and cleaning solvents. Though considerably more expensive than stove oil, they are still economical where they can be used in place of hand labor.

SELECTIVITY THROUGH THE SOIL

The selective herbicides discussed above have all been contact sprays that produce selective action on the tops of plants. Many compounds having the properties of soil sterilants act selectively upon plants through the roots; in fact selectivity among plants is commonly manifested, and only when heavy dosages are used is sterilization against all weeds obtained.

With sterilants of the volatile type, loss of vapor from the top soil may result in selectivity. For instance, with carbon disulfide one may destroy the wild morning-glory in an area without killing Bermuda grass, which is relatively shallow-rooted. Such a treatment might be used to kill deep-rooted perennials in a Bermuda grass lawn.

In the use of the temporary sterilant sodium chlorate, selectivity may follow from localization of the chemical in the soil, or it may result from a chemical tolerance shown by certain plants of saline regions. Of the first type is the killing of Johnson grass by a winter application of chlorate to the soil, and the survival of wild morning-glory in the same area; the chemical becomes diluted before it can percolate to the deep roots of the latter pest. Another instance, noted many times, is the survival of poison oak (*Rhus diversiloba*) on firebreaks where chlorate has been used alone or in combination with arsenic to control bearmat (*Chamaebatia foliolosa*) and other shallow-rooted perennials.

As an example of chlorate tolerance, salt grass (*Distichlis spicata*) cannot be eradicated easily by this chemical although Bermuda grass (*Cynodon dactylon*), Russian knapweed (*Centaurea repens*), and other perennials growing on the same area will be killed. Alkali-tolerant weeds such as salt-bush (*Atriplex semibaccata*), bractscale (*A. bracteosa*), and spikeweed (*Centromadia pungens*) are usually the first weeds to reappear where chlorate has been used to kill Johnson grass (*Holcus halepensis*), wild morning-glory (*Convolvulus arvensis*), or other perennials.

Despite the extreme toxicity of arsenic, certain weed species, notably bractscale, yellow star thistle, salt grass, and similar salt-tolerant pests, may grow where the soil has been made completely sterile to other plants.

Borax has an advantage over chlorate and arsenic, in that grasses are stimulated by intermediate concentrations (6 lbs. per square rod) of it in the soil (17). The same concentrations are toxic to St. Johnswort (*Hypericum perforatum*) and bearmat. After borax application for control of these pests, grasses usually invade the treated areas to the total exclusion of the weeds, and growth is often more vigorous than on normally weed-free grass areas. Because selective chemicals may thus shift vegetation types, conceivably they might find extensive use in range-improvement work.

GROWTH-REGULATING SUBSTANCES AS SELECTIVE WEED KILLERS

A wholly new field in chemical weed control has been opened by the discovery that plant-growth-regulating substances may be used as selective weed killers—a discovery made in Britain in 1942 by SLADE, TEMPLEMAN,

and SEXTON (18) and in this country in 1944 by BEAL (2), MITCHELL and HAMNER (15), and HAMNER and TUKEY (9). As these workers have shown, cereal and grass crops exhibit considerable tolerance for this type of chemical, whereas most broad-leaved plants, including many weed species, are highly susceptible. Consequently, the growth regulators can be used selectively to control broad-leaved weeds in cereal crops, pastures, lawns, and elsewhere.

Furthermore, selective action is shown by the roots from application of the chemical to the soil, as well as by the tops after a spray application on the foliage. The outstanding feature of this growth-regulating type of chemical is its extreme toxicity; satisfactory control of mustard species has been secured with $\frac{1}{2}$ to 1 pound per acre, and BLACKMAN (3) reports almost complete control of *Brassica arvensis* in the seedling stage with 4 ounces per acre applied as a spray. Cereal crops produce increased yields through lack of competition with the weeds.

After being sprayed on, the growth regulators are absorbed through the leaves. They are translocated apparently in the same way as naturally occurring plant hormones; that is, in a polar fashion from foliage to roots. Being toxic, they will kill the perennial root systems of many weeds such as wild morning-glory, Canada thistle (*Cirsium arvense*), dandelion (*Taraxacum vulgare*), and plantain. They can therefore be used to control practically all broad-leaved weeds in lawns, pastures, and cereal and grass crops. They are valuable against poison ivy (*Rhus toxicodendron*), poison oak, poison sumac (*Rhus vernix*), Japanese honeysuckle (*Lonicera japonica*), and similar pests in pasture or woodland areas. Recent tests indicate their use in eliminating cattails (*Typha* spp.), tules (*Scirpus* spp.), bur-reed (*Sparganium eurycarpum*), willows, and other weeds of wet lands and drainage channels (11). Chief among such chemicals are the phenoxyacetic acid derivatives. In Britain the 4 chloro-2 methyl compound has found most favor; in this country the 2,4 dichloro compound. Both the phenoxy and naphthoxy compounds are effective, and the sodium and ammonium salts of the acetic acid derivatives have been used.

Although the growth regulators show their greatest selectivity between grasses and broad-leaved species, other plants display varying susceptibilities to their toxic action. Weeds as well as crop plants differ, and some differences occur among the grasses. Table VII lists a number of weeds whose reaction to growth regulators has been noted. In using this table one should remember that small seedlings are easier to kill than mature plants; that perennials in active growth are more susceptible than when old and woody; and that the form of the chemical, the dosage, and the method of application may affect the result.

Woody plants sprayed in July and August by HAMNER and TUKEY (9) developed growth curvatures; the leaves dropped off, and the stem tips were killed. As those workers note, treatment earlier in the season may give more drastic results.

In instances where the same species were involved, results of tests in California substantially agree with those cited above. The California observations have been made on plot tests where 2,4-D (2,4 dichlorophenoxyacetic

TABLE VII

WEEDS THAT HAVE PROVED SUSCEPTIBLE OR RESISTANT TO GROWTH REGULATORS*

INTERMEDIATE SPECIES	REFERENCE	INTERMEDIATE SPECIES	REFERENCE
<i>Alsine (Stellaria) media</i>	22	<i>Leptilon canadense</i>	22
<i>Anthemis cotula</i>	22	<i>Oxalis corniculata</i>	23
<i>Cardaria</i> spp.	23	<i>Plantago major</i>	22
<i>Chenopodium album</i>	22	“ <i>rugelii</i>	22
“ <i>glaucum</i>	22	<i>Polygonum aviculare</i>	22, 23
<i>Euphorbia maculata</i>	23	<i>Rumex Acetosella</i>	23
<i>Hypericum perforatum</i>	23	<i>Solidago</i> spp.	23
<i>Lactuca scariola</i>	22	<i>Tragopogon pratensis</i>	22
“ spp.	22	<i>Typha latifolia</i>	23
RESISTANT SPECIES	REFERENCE	RESISTANT SPECIES	REFERENCE
<i>Achillea millefolium</i>	14, 22, 23	<i>Matricaria inodora</i>	3
<i>Agropyron repens</i>	9	<i>Muhlenbergia schreberi</i>	22
<i>Agrostema githago</i>	22	<i>Oxalis corniculata</i> var.	
<i>Alchemilla arvensis</i>	3	“ <i>atropurpurea</i>	11, 22, 23
<i>Anthemis cotula</i>	18, 23	<i>Persicaria persicaria</i>	22
<i>Asclepias speciosa</i>	23	“ <i>pennsylvanicum</i>	22
<i>Atriplex patula</i>	3	<i>Physalis</i> spp.	23
<i>Avena fatua</i>	9, 11	<i>Plantago major</i>	14
“ <i>sativa</i>	18	<i>Poa annua</i>	11
<i>Bromus mollis</i>	11	“ <i>pratensis</i>	9
“ <i>rigidus</i>	11	<i>Polygonum aviculare</i>	3
<i>Cenchrus pauciflorus</i>	22	“ <i>convolvulus</i>	22
<i>Centaurea repens</i>	11, 23	“ <i>tartaricum</i>	22
<i>Cephalanthus occidentalis</i>	23	<i>Pteris aquilina</i>	3, 23
<i>Chaetocloa</i> spp.	22	<i>Rhus diversiloba</i>	23
<i>Chrysanthemum leucanthemum</i> var. <i>pinnatifidum</i>	14	<i>Rubus procerus</i>	11
<i>Cynodon dactylon</i>	11	“ spp.	14, 23
<i>Digitaria ischaemum</i>	9	<i>Rumex acetosella</i>	14, 22
<i>Digitaria (Syntherisma) sanguinale</i>	9, 22	“ <i>obtusifolius</i>	14
<i>Echinocloa crus-galli</i>	9, 22	“ spp.	3, 22
<i>Elusine indica</i>	9, 22	<i>Salsola pestifer</i>	22
<i>Equisetum</i> spp.	22	<i>Saponaria vaccaria</i>	22
<i>Euphorbia esula</i>	22	<i>Senecio jacoboea</i>	23
<i>Fumaria officinalis</i>	3	<i>Setaria lutescens</i>	9
<i>Helxine soleitroli</i>	11	“ <i>viridis</i>	9
<i>Holcus halepensis</i>	11	<i>Sida hederacea</i>	11, 23
<i>Hordeum jubatum</i>	22	<i>Silene noctiflora</i>	22
<i>Linaria vulgaris</i>	23	<i>Solanum nigrum</i>	22
<i>Lolium multiflorum</i>	11	“ <i>rostratum</i>	22
<i>Lychnis alba</i>	22	<i>Urtica dioica</i>	3
<i>Matricaria chamomilla</i>	3	<i>Verbascum thapsus</i>	22
		<i>Viola</i> spp.	22
SUSCEPTIBLE SPECIES	REFERENCE	SUSCEPTIBLE SPECIES	REFERENCE
<i>Amaranthus blitoides</i>	22, 23	<i>Artemisia vulgaris</i> var.	
“ <i>caudatus</i>	11	<i>heterophylla</i>	22
“ <i>retroflexus</i>	9, 14, 22, 23	<i>Asclepias syriaca</i>	9
<i>Ambrosia artemisiifolia</i>	9, 22	<i>Barbarea barbarea</i>	22
“ <i>psilostachya</i>	11, 23	<i>Brassica arvensis</i>	3, 22
<i>Apocynum cannabinum</i>	23	“ <i>junceae</i>	22
<i>Arctium minus</i>	22, 23	“ <i>napus</i>	22

TABLE VII (Continued)

WEEDS THAT HAVE PROVED SUSCEPTIBLE OR RESISTANT TO GROWTH REGULATORS*

SUSCEPTIBLE SPECIES	REFERENCE	SUSCEPTIBLE SPECIES	REFERENCE
<i>Brassica nigra</i>	11	<i>Melilotus alba</i>	9
“ <i>sinapis visiani</i>	19	“ spp.	22, 23
“ spp.	23	<i>Neslia paniculata</i>	22
<i>Camelina</i> spp.	22	<i>Oxalis</i> spp.	14
<i>Capsella</i> (<i>Bursa</i>) <i>bursa-</i> <i>pastoris</i>	14, 22, 23	<i>Papaver Rhoeas</i>	3, 18
<i>Cardaria draba</i> var. <i>repens</i> ..	11	<i>Plantago lanceolata</i>	9, 14, 22
<i>Centaurea cyanus</i>	3	“ <i>major</i>	9, 18
“ <i>solstitialis</i>	11, 23	“ spp.	23
<i>Cerastium vulgatum</i>	22	<i>Polygonum aviculare</i>	14
<i>Chenopodium album</i>	9, 18, 23	“ <i>coccineum</i>	11
<i>Chrysanthemum segetum</i>	18	“ <i>convolvulus</i>	3
<i>Cichorium intybus</i>	11, 23	“ <i>pennsylvanicum</i>	9
<i>Cicuta</i> spp.	23	<i>Portulaca oleracea</i>	9, 23
<i>Cirsium lanceolatum</i>	23	<i>Potentilla</i> spp.	22
<i>Conium maculatum</i>	11, 23	<i>Prunella vulgaris</i>	23
<i>Conringia orientalis</i>	22	<i>Ranunculus arvensis</i>	3, 18
<i>Convolvulus arvensis</i>	9, 11, 23	<i>Raphanus raphanistrum</i>	3, 18
“ <i>sepium</i>	14	“ <i>sativus</i>	23
<i>Datura stramonium</i>	14	<i>Roripa austriaca</i>	23
<i>Daucus Carota</i>	23	<i>Rumex acetosella</i>	11
<i>Eichornia crassipes</i>	11	“ <i>crispus</i>	23
<i>Equisetum</i> spp.	3, 11	<i>Salix</i> spp.	23
<i>Erysimum cheiranthoides</i>	3, 22	<i>Scandix pecten veneris</i>	3
<i>Euphorbia maculata</i>	11, 22	<i>Scirpus acutus</i>	11, 23
<i>Foeniculum vulgare</i>	11, 23	<i>Setellaria media</i>	9, 14
<i>Galeopsis tetrahit</i>	3	<i>Silybum marianum</i>	11, 23
<i>Glechoma hederacea</i>	22	<i>Sisymbrium altissimum</i>	22
<i>Helianthus annuus</i>	22	<i>Solidago occidentalis</i>	11
<i>Hydrocotyl prolifera</i>	11	<i>Sonchus arvensis</i>	9
“ <i>rotundifolia</i>	14	“ <i>asper</i>	23
“ <i>umbellata</i>	23	“ <i>oleraceus</i>	23
<i>Hypericum perforatum</i>	11	<i>Sophis</i> spp.	22
<i>Hypochoeris radicata</i>	23	<i>Sparganium eurycarpum</i>	11, 22
<i>Iva xanthifolia</i>	22	<i>Spergula arvensis</i>	3, 18
<i>Jussiaea californica</i>	11	<i>Taraxacum officinale</i>	9, 11, 14, 22, 23
<i>Kochia scoparia</i>	22	<i>Thlaspi arvense</i>	3, 18, 22, 23
<i>Lactuca pulchella</i>	23	<i>Tribulus terrestris</i>	22
“ <i>scariola</i>	23	<i>Trifolium repens</i>	11
<i>Lamium amplexicaule</i>	22	<i>Urtica</i> spp.	23
<i>Lappula echinata</i>	22	<i>Verbena bracteata</i>	22
<i>Lepidium apetalum</i>	22	<i>Veronica hederifolia</i>	3
“ <i>virginicum</i>	22	“ spp.	22
<i>Malva parviflora</i>	23	<i>Xanthium canadense</i>	23
“ <i>rotundifolia</i>	9, 22, 23	“ <i>spinosum</i>	23
<i>Medicago lupulina</i>	22, 23	“ spp.	22

* It is impossible to separate plants into distinct groups with respect to their reaction to growth regulators. Some of the plant species included here were tested as seedlings treated through the soil; others were sprayed as young or mature plants. Differences of opinion found in this table undoubtedly result from such differences in testing methods. This grouping represents interpretation by the writer of descriptions of experiments published by the workers cited. Materials used in the various tests reported include 2,4-dichlorophenoxyacetic acid and its sodium salt in this country, and 4 chloro-2 methyl phenoxyacetic acid and its sodium salt in Britain.

acid or its salts) solutions have been applied to weeds growing in the field. The weed species include several biennials and perennials, and the obser-

vations involve results of translocation as well as contact toxicity. Concentrations of 0.2 and 0.1 per cent. were used, and most of the plants were large and actively growing when treated. Seedlings have proved somewhat easier to kill; plants in the late-blossom and seed-forming stages, more difficult.

This listing of species susceptible and resistant to the action of 2,4-D is a useful index to the weeds that may be treated successfully. It is helpful also in indicating the possibility of selectivity in the control of weeds in crops.

Discussion and summary

Selective killing of certain plant species from mixed plant populations is a common phenomenon, and selectivity is based upon many differences. Among these are differences in wettability, in exposure of essential plant parts such as meristems, in orientation and distribution of leaves, in depth and distribution of roots, and in chemical tolerance to certain toxic substances. This last type is probably the most promising in selective weed control because methods based on chemical tolerance depend largely upon composition of the herbicidal material and stage of growth of the plants—factors that can be regulated. Wettability, on the other hand, may be largely determined by plant characteristics or by weather conditions before and during treatment. Exposure as related to orientation and distribution of plant parts is also beyond control, being inherent in the crop or weed species involved.

Introduction of the dinitro compounds, the selective oils, and the growth-regulating compounds has greatly enlarged the field for selective control of weeds. New crops have been added to the list of resistant species, and more will be found in the future. Although increases in toxicity and reduction in costs may even yet be effected, greatest promise lies in the broadening of selectivity and in the discovery of new crops that submit to selective herbicidal action.

Among crop plants, the Cruciferae present one group that should receive attention.

The experimental killing of grass seedlings in wild mustard with an oil fraction should offer a good lead to follow. The beet and mangel crops are another important group, and composites of the lettuce type represent a third. The control of weedy grasses in these broad-leaved crops would be a real advance; and the use of oil fractions warrants trial, since oils seem particularly toxic to grasses.

The dinitro substituted phenols have received detailed study but further exploratory work with them, seeking new crop-weed specificities, seems justified. Some work on the chlorinated phenols indicates that pentachlorophenol and its salts deserve further consideration. Ammonium pentachlorophenate offers possibilities as a noncolored selective spray (7) and pentachlorophenol is useful as a fortifying agent in oils and oil emulsions.

The growth regulators offer another great opportunity for testing selectivity. Although broad-leaved plants seem most susceptible to their action

and grasses generally tolerant, results of testing already show a wide difference among the former group and some variation among the latter. It seems possible that further testing of these compounds in their various combinations may disclose new and useful specificities among weeds and crops.

Dozens of growth regulators have already been tried, and many more will undoubtedly be synthesized. Since most of these are acids in their parent form, each offers opportunity to form metallic salts, esters, amides, and the like; almost innumerable compounds can be synthesized for testing. The systematic study of the toxicity and selectivity of these compounds offers a great opportunity for practical and scientific application of biochemistry and plant physiology in the service of agriculture.

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